

X-RAY ABSORPTION SPECTROSCOPY OF POROUS MATERIALS

Mojca Rangus¹, Matjaž Mazaj¹, Nataša Novak Tušar^{1,2}, Nataša Zabukovec Logar^{1,2}

¹National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

²University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

E-mail: mojca.rangus@ki.si

ABSTRACT

X-ray absorption spectroscopy is ideal for studying the structure of ordered or disordered samples since it views the matter on the atomic level. Its main advantage is the sensitivity to the local chemical environment of the observed atoms which act as probes that detect their surroundings. It can therefore be successfully used for studying various types of porous materials, such as zeolites, mesoporous silicates or metal-organic frameworks. In this contribution we will focus on materials synthesized in the Laboratory of Inorganic Chemistry and Technology at National Institute of Chemistry, which include various types of MOFs and a disordered mesoporous silica KIL-2.

Keywords: XAS, EXAFS, XANES, metal-organic frameworks, porous materials.

INTRODUCTION

The term porous materials denotes a broad range of inorganic or organic materials that can be crystalline or amorphous with a system of pores that can be ordered or disordered. Many types of different porous solids are known; from inorganic which include zeolites, aluminophosphates, mesoporous silicates and other zeolite related materials, inorganic-organic materials such as metal organic frameworks (MOFs), and organic, which among others include porous polymers, carbons, etc.

MOFs are crystalline solids that have inorganic building units covalently bonded to organic molecules, typically polycarboxylates, to form three-dimensional structures with different porosities [1]. The ability to precisely design the structure of MOFs for specific applications, such as for gas storage and separation, catalysis, drug delivery, batteries, etc., is considered to be one of their most important advantages [2]. Unfortunately, MOFs very often exhibit relatively low hydrothermal stability, which might limit their use in storage systems.

KIL-2 has a high specific surface area can be used successfully as a catalytic support for immobilizing catalytically active metals, such as iron (FeKIL-2) [3] or manganese (MnKIL-2) [4] or metal oxides (CuFeKIL-2) [5,10]. KIL is a group of materials first synthesized at the National Institute of Chemistry in Ljubljana (Kemijski Inštitut Ljubljana—KIL) [5]. It is composed of agglomerated silica nanoparticles and has interparticle porosity. FeKIL-2 is low cost and has also proven to be a highly efficient catalyst for the removal of VOCs; it also shows great potential for water [4] and air purification applications [3].

X-ray absorption spectroscopy (XAS) is a technique which enables us to study the local structure around a selected type of atoms that are present in a material. In X-ray absorption a photon is absorbed by the atom, exciting (ejecting) an electron from a core level (photoeffect). A huge advantage of XAS is that it does not need a long-range order since it probes the local

surroundings of an atom. XAS can therefore be applied not only to crystals, but also to materials with little or no long range order such as amorphous solids, glasses, thin films, membranes, solutions, liquids or even gases.

For a successful characterization of a newly synthesized material or for the study of structure transformations, it is often necessary to study sites in a material that do not appear periodically – in the material there is no long range order. Sometimes the crystals are of nanometre size or the particles have an unordered structure. Special cases represent liquid samples and reaction gels. These are the examples where the well-established diffraction techniques, such as XRD, do not work, since they need a long range order to be able to give some structural information about the material. It is quite the opposite with the spectroscopic techniques and they offer a detailed insight in the structure on the atomic level. Their main advantage is the sensitivity to local chemical environment of the observed atoms, which act as probes that detect the surroundings. XAS is able to distinguish the type of the neighboring atoms and can detect their relative distances to the observed atoms or nuclei. It also probes the degree of local order or disorder. Since the measurements are in most cases rapid they enable the investigation of unstable or very diluted samples. No need for long range order facilitates the study of amorphous samples, nanometre-scale crystals, thin films, liquids and gases, etc.

EXAMPLE 1: Investigation of the MIL-45(Fe) and MIL-100(Fe) crystallization process

XAS was used to study the crystallization process of two iron containing MOFs, MIL-45 and MIL-100 [6]. The final structure that was obtained depends only on a single synthesis parameter – the solvent composition, while all other variables (time, temperature, molar ratios) were kept constant. Crystallization process was studied ex-situ with XAS. By analyzing the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) parts of the Fe K- edge absorption spectra we were able to identify the connectivity of iron atoms and the phases formed at different stages of the synthesis. In the investigated case the composition of the solvent influences not only the framework type but also the valence state of iron ions in the final materials. The studied system gives us a unique opportunity to study how formation mechanisms depend upon a single synthesis parameter as well as observe the whole crystallization process. With the knowledge gained by studying the formation and crystallization mechanisms of increasingly popular metal organic frameworks, we could design materials for a specific function or application.

EXAMPLE 2: Structural transformations of Ca-based MOF upon thermal treatment and hydration

We focused our research on structural dynamics of Ca-benzendicarboxylate (Ca-BDC(RT)) [7,8] which possesses topology of MIL-53. MIL-53 is a very well-known and extensively researched MOF which is known for its framework flexibility and "breathing effect". However, Ca-BDC(RT) does not show any breathing effect upon heating or hydration. Instead, it undergoes significant crystal-to-crystal transformations leading to the new non-porous phases. Ca-BDC(RT) material is built up from chains of edge-sharing polyhedra with Ca²⁺ centers with 8-fold coordination. Ca²⁺ cations are coordinated to six framework oxygen atoms and the

remaining two oxygen atoms come from water and DMF molecules, respectively. During heating Ca-BDC(RT) framework undergoes two phase transitions. First structural change to Ca-BDC(150) at 150 °C causes breaking of Ca-O(H₂O) and Ca-O(DMF) bonds and leads to the non-uniform phase transition with either two separate phases or two types of domains within the crystals. In this step DMF molecules diffuse from the outer parts of the crystals and the domains are transformed to the non-porous Ca-BDC(400) phase, which prevents the removal of DMF from the cores of the crystals, disables their transformation and allows only minor subsiding of the channels. Heating to 400 °C triggers a complete transformation into Ca-BDC(400) phase. It removes the coordinated water and the remaining DMF molecules from the crystal cores and consequently the coordination number of Ca²⁺ is reduced to 6. However, due to its ionic radius (106 pm), Ca²⁺ prefers higher coordination number than 6. Thus in MOFs, Ca cations in octahedral environment have high tendency for additional ligand bonding (typically water molecules). Indeed, Ca-BDC(400) is stable only at elevated temperatures, inert atmosphere or in vacuum. In humid environment Ca²⁺ will coordinate to additional three water molecules and transform to Ca-BDC(400)hyd [9] with 9-fold coordination of Ca²⁺. The structural changes upon hydration/dehydration were found to be reversible.

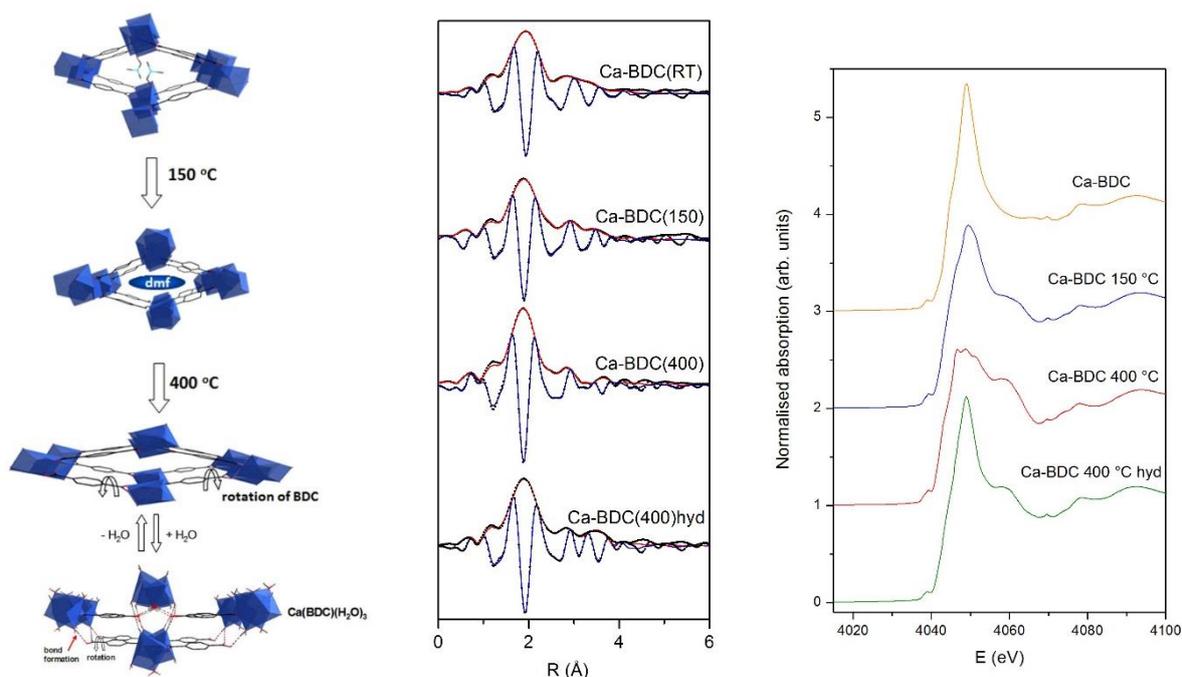


Figure 1. Schematic representation of structural transformations of Ca-terephthalate from Ca-BDC(RT) to Ca-BDC(400)hyd (left). The k^3 -weighted Fourier transformed Ca K-edge EXAFS (middle) and XANES (right) spectra of Ca-BDC(RT), Ca-BDC(150), Ca-BDC(400) and Ca-BDC(400)hyd.

EXAMPLE 3: Characterization of Cu-Fe mixed-oxide functionalized silica catalysts

The aim was to explain how the amount of Fe in the samples influences the catalytic performance of the Cu-Fe mixed-oxide catalyst immobilized on mesoporous KIL-2 support [10]. The Cu-Fe structure correlation was studied by XAS. EXAFS data of the samples and the best fit models describe the short-range order of the Cu atoms in terms of neighbors, distances and thermal and static disorder. Cu K-edge EXAFS spectra of 100CuKIL-2 and CuFeKIL-2 samples show a gradual change from CuO (in 100CuKIL-2) to a different Cu containing

compound (Cu_{0.5}FeKIL-2), with an increasing amount of Fe in the studied silicas. We presume that via the solid-state thermal conversion of Cu precursor on FeKIL-2 samples, the Cu interacts with Fe and forms a copper iron oxide. To characterize this newly formed compound, we analyzed the local environment of Cu in the sample containing the highest amount of Fe, Cu_{0.5}FeKIL-2. Since the EXAFS spectra of both Cu_{0.2}FeKIL-2 and Cu_{0.5}FeKIL-2 samples are indistinguishable, it is safe to assume that all the Cu in the Cu_{0.5}FeKIL-2 sample is coordinated to Fe. We found that only a cuprospinel structure (CuFe₂O₄) gave a good agreement between the fit and the measured Cu K-edge EXAFS spectrum.

CONCLUSION

We hope to show that the X-ray absorption spectroscopy can be successfully used for characterization of porous materials as well as the studies of their crystallization and structural transformation processes.

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